

Observable indicators of the sensitivity of PM_{2.5} nitrate to emission reductions—Part II: Sensitivity to errors in total ammonia and total nitrate of the CMAQ-predicted non-linear effect of SO₂ emission reductions

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Abstract

The inorganic aerosol system of sulfate, nitrate, and ammonium can respond non-linearly to changes in precursor sulfur dioxide (SO₂) emissions. The potential increase in nitrate, when sulfate is reduced and the associated ammonia is released, can negate the sulfate mass reduction. Current regional-scale air quality models do not reproduce the present-day levels of total ammonia and total nitrate, leading to possible errors in the air quality model predictions of future nitrate concentrations. The objective of this study is to quantify the effects of errors in the total-ammonia and total-nitrate budgets on nitrate relative response (RR), defined as the percent change in particulate nitrate stemming from reductions in SO₂ emissions. This objective is addressed through three sensitivity studies using the Community Multiscale Air Quality model (CMAQ). These studies assess the sensitivity of the nitrate RR (%) to (1) errors in ammonia emissions, (2) errors in the heterogeneous production of nitrate from N₂O₅, and (3) errors in the NO_x emissions. The results indicate that nitrate RRs due to SO₂ emission reductions are much more sensitive to errors in the total-ammonia budget than to errors in the total-nitrate budget. The sensitivity of the nitrate RR to NO_x emissions is only moderate and is due primarily to the effect of NO_x changes on sulfate production, rather than on total nitrate. Also, a strong relationship was found between the nitrate RR and the Adjusted Gas Ratio (free ammonia adjusted for the degree of sulfate neutralization divided by total nitrate).

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1. Introduction

Emission reductions being proposed as a first step toward attaining the annual-average PM_{2.5} standard focus on control of inorganic PM precursors in the eastern United States (<http://www.epa.gov/interstateairquality/>), where inorganic components

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make up a significant fraction of the aerosol mass. The inorganic aerosol system of sulfate, nitrate, and ammonium can respond non-linearly to changes in precursor emissions (Seinfeld and Pandis, 1998, p 538). One non-linear response of concern is the potential increase in nitrate when sulfate is reduced: two ammonia molecules are released for each $(\text{NH}_4)_2\text{SO}_4$ molecule “removed”; if that ammonia combines with nitric acid to yield two molecules of particulate NH_4NO_3 , then the total particulate mass would increase despite the sulfur dioxide (SO_2) emission reduction (Ansari and Pandis, 1998; West et al., 1999; Blanchard et al., 2000).

It is a challenge for regional-scale air quality models to reproduce present-day aerosol concentrations (Seigneur, 2001; Boylan et al., 2002; Mebust et al., 2003; Eder and Yu, 2006), yet they are the most comprehensive framework available for predicting the non-linear effects of emission controls on future ambient aerosol concentrations. To take advantage of this framework while acknowledging its imperfections, US policymakers use air quality models mainly for calculating relative reduction factors (RRFs) (US EPA, 2007). In the context of $\text{PM}_{2.5}$ control, RRFs are defined as the multiplicative factors by which the present-day concentration of a given $\text{PM}_{2.5}$ component (e.g., sulfate) measured at a given location and during a given season will change in response to an emission-reduction policy. To project the $\text{PM}_{2.5}$ mass concentrations expected after completion of a proposed emission reduction, the present-day ambient concentration of each chemical component of $\text{PM}_{2.5}$ is multiplied by its respective RRF and the adjusted components are then combined (US EPA, 2007). Note that the word “reduction” in the RRF acronym can be a misnomer in cases where, for example, the particulate nitrate increases due to a sulfate reduction. In this paper, we find it more illustrative to express model projections of nitrate in terms of percent changes rather than multiplicative factors. Thus, we use the acronym relative response (RR) to signify the relative *response* in concentration expressed as a percent; an RR (%) may therefore be positive or negative.

In modeling, a major obstacle to accurately reproducing present-day particulate nitrate concentrations is the large uncertainty in the total budgets (gas + particulate) of ammonia, sulfate (Yu et al., 2005), and nitrate. Of the three, the sulfate budget in the eastern US is characterized reasonably well, as corroborated by regional comparisons of modeled and observed sulfate concentrations (Eder and Yu, 2006). An important question is “Do the inaccura-

cies in total-ammonia and total-nitrate budgets significantly affect the nitrate RRs predicted by air quality models?” The primary objective of this study is to quantify the sensitivity of nitrate RRs to errors or uncertainties in present-day total-ammonia and total-nitrate budgets. In the remainder of this paper, the term “nitrate RR” represents the nitrate RR that is predicted to result from a 25% SO_2 emission reduction imposed uniformly across the study domain.

In the analysis that follows, we first describe the setup of the modeling study, and explore the attributes of the monthly averaged nitrate RR in the base-case simulation results for the eastern US in January 2002. Next, the ranges of the three input uncertainties—one for total ammonia and two for total nitrate—are developed. Finally, we describe the results of the three sensitivity studies and compare the relative importance of each input uncertainty on the nitrate RR.

2. Modeling methodology

Version 4.4 (2004 release) of the Community Multiscale Air Quality model (CMAQ) is used with the SAPRC99 gas-phase chemical mechanism and the ISORROPIA v1.5 inorganic equilibrium module (<http://nenes.eas.gatech.edu/ISORROPIA/>). ISORROPIA is run with the metastable state option assuming the inorganic aerosol phase is always in aqueous solution. Under most conditions encountered in the wintertime across the eastern United States, this assumption is more appropriate than the stable option which permits the formation of inorganic salts (Rood et al., 1989; Khlystov et al., 2005). Meteorological inputs are identical to those described and evaluated by Gilliam et al. (2006) except that 24 vertical layers are used instead of 14. The same set of meteorological inputs is used for all CMAQ simulations described herein. Emissions are based on version 3 of the EPA 1999 National Emission Inventory (NEI) grown to 2002 for mobile on-road and to 2001 for area sources. With slow economic growth, the difference between 2001 and 2002 is negligible. Emissions from electric generating units are based on 2002 continuous emissions monitoring data (<http://cfpub.epa.gov/gdm/>) and with NH_3 emissions adjusted similarly to the inverse-modeling-based recommendations of Gilliland et al. (2006). The NH_3 inverse modeling is designed to bring the total-ammonia emissions, losses, and transformations into domain-wide

balance with measured concentrations, but have the added benefit of mitigating large errors in the total-nitrate budget (Gilliland et al., 2003). The continental US domain is discretized with a horizontal grid cell size of 36 km (see Fig. 1) and 24 vertical layers from ground level to 16 km. The first layer is nominally 38 m in thickness. The 36 km grid dimension is considered adequate for the present analysis because the relevant species, except ammonia, are formed by secondary atmospheric processes.

A winter period is chosen for the study because in cold temperatures, particulate nitrate is most abundant and the thermodynamic equilibrium relationships are more linear (Pinder et al., this issue) and because preliminary simulations demonstrated that the replacement of sulfate by nitrate is approximately eight times larger in winter than in summer. CMAQ simulations are performed for the month of January 2002 to correspond to the EPA Supersites Program intensive data collection period. All concentrations reported in this paper reflect monthly average values to approximate the time scale at which RRFs are typically calculated (US EPA, 2007). All RRs are computed from a pair of CMAQ-simulated monthly average species concentrations (one with and one without the 25% SO₂ emission reduction) given in Eq. (1) as follows:

$$\text{Nitrate RR} = \frac{[\text{NO}_3^-]_{\Delta\text{SO}_2} - [\text{NO}_3^-]_{\text{base}}}{[\text{NO}_3^-]_{\text{base}}} \times 100. \quad (1)$$

Because PM_{2.5} is a health concern, this analysis focuses on areas in the eastern US that are relatively polluted with regard to inorganic particulate matter (see Fig. 1). Polluted cells are defined as those with dry inorganic PM_{2.5} ≥ 5 μg m⁻³. The area so defined covers a large fraction of the eastern US yet cuts off the southernmost portion of the Southeast and much of West Virginia and Maine. A total of 1822 ground-level CMAQ cells in the eastern US meet the selection criteria and only these cells are considered in the subsequent analyses.

3. Base-case characterization

The distribution of particulate nitrate concentrations is a factor of 2 broader than that of sulfate (see Fig. 2a and b). When paired by cell, nitrate concentrations are larger than sulfate in 80% of the cells and more than 2 times larger than sulfate in 37% of the cells. After imposing a 25% reduction on SO₂ emissions, the sulfate response is damped (see Fig. 2c). The relative reduction in particulate sulfate is centered at only ~13.5%, with the smaller reductions in the upper Midwest (10–11%) and the larger ones in the Southeast (14–15%). The damped sulfate response is due to an oxidant limitation in the aqueous-phase production of sulfate at current levels of SO₂ emissions in the eastern US; the gas-phase production of sulfate, on the other hand, responds linearly to the SO₂ emission reduction.

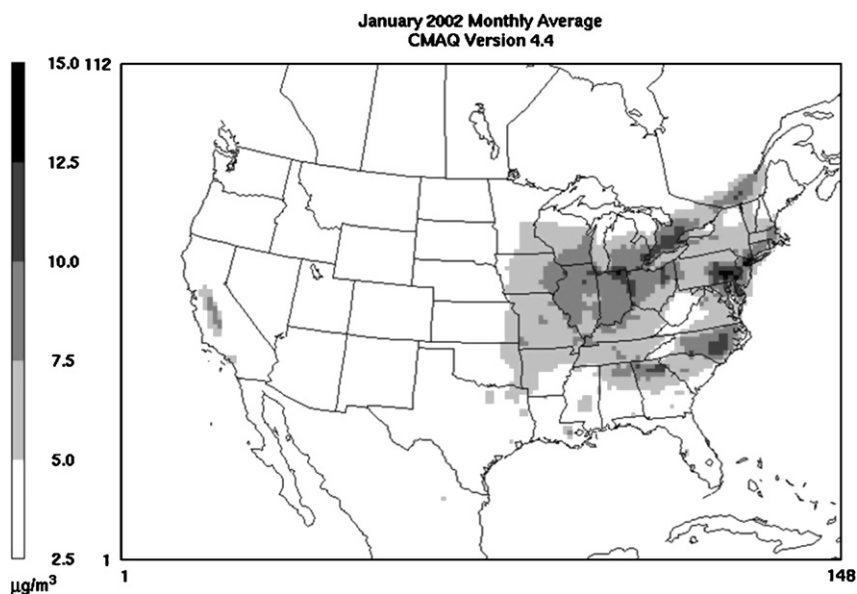


Fig. 1. Map of CMAQ 36 km domain with shaded cells demarcating the regions where CMAQ-simulated monthly average inorganic PM_{2.5} ≥ 5 μg m⁻³ in January 2002.

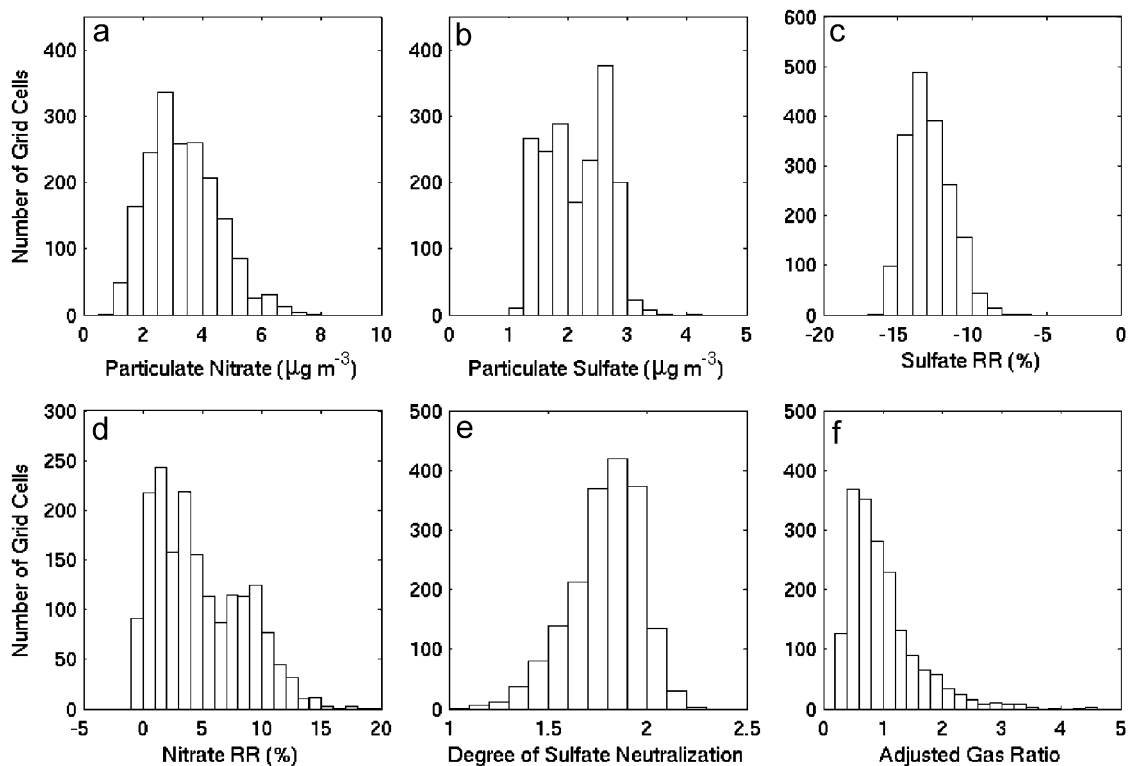


Fig. 2. Frequency distributions of (a) particulate NO_3^- concentrations, (b) SO_4^{2-} concentrations, (c) SO_4^{2-} RR, (d) NO_3^- RR, (e) DSN, and (f) AdjGR, using base-case simulation results in the 1822 selected cells.

The oxidant limitation is accentuated in winter due to the lack of isoprene emissions from deciduous trees during senescence. The CMAQ sulfate-tracking model indicates that a majority of the wintertime ambient particulate sulfate is produced by aqueous processes despite the oxidant limitation.

Although the relative change in sulfate exhibits very little spatial variation, the nitrate RR in the base case varies from -0.5% to 15.5% (compare Fig. 2c and d). Thermodynamic calculations by Pinder et al. (this issue) show that this broad variation in nitrate response may be explained by the Adjusted Gas Ratio, defined as follows:

$$\begin{aligned} \text{AdjGR} &= \frac{\text{Free ammonia}}{\text{Total nitrate}} = \frac{\text{NH}_X - \text{DSN} \times \text{SO}_4^{2-}}{\text{TNO}_3} \\ &= \frac{[\text{NH}_3] + [\text{NO}_3^-]}{[\text{HNO}_3] + [\text{NO}_3^-]}, \end{aligned} \quad (2)$$

where total ammonia is termed $\text{NH}_X = \text{NH}_3(\text{g}) + \text{NH}_4^+(\text{p})$, and total nitrate is termed $\text{TNO}_3 = \text{HNO}_3(\text{g}) + \text{NO}_3^-(\text{p})$. The degree of sulfate neutralization (DSN) is defined operationally as $[\text{NH}_4^+ - \text{NO}_3^-] / \text{SO}_4^{2-}$. A DSN of 2 indicates full

neutralization. A DSN of 1 indicates the sulfate is, on average, ammonium bisulfate. At most locations in the modeling domain the ammonium concentrations are insufficient to neutralize sulfate completely (see Fig. 2e).

At AdjGR values much greater than 1, the system is ammonia-rich and little replacement of sulfate by nitrate is expected because there is insufficient nitric acid to react with the ammonia released by each sulfate ion (i.e., “non-replacement regime”). At AdjGR values much less than 1, the system is ammonia-limited and particulate nitrate is expected to increase in response to the sulfate reduction (i.e., “replacement regime”). At AdjGR values close to 1, the particulate nitrate response to a sulfate reduction is expected to transition between the non-replacement and replacement regimes (i.e., “transition regime”). This explanation is most accurate when particulate nitrate concentrations are more than a few tenths of a microgram per cubic meter.

The relationship between the AdjGR and nitrate RR (an S-shaped sigmoid function) is given by

Eq. (3) and illustrated in Fig. 5 of Pinder et al. (this issue).

$$\text{Nitrate RR} = \frac{14.892}{1 + \exp(2.746 \log \text{AdjGR} - \log 0.588)} \quad (3)$$

Eighty-eight percent of the cells have an AdjGR between 0.4 and 2.0, with a mode at AdjGR = 0.6 (see Fig. 2f). Thus, much of the eastern US is in the “transition regime”, consistent with the broad range of nitrate RRs predicted by CMAQ. The nitrate RR is close to zero in the non-replacement regime (i.e., AdjGR \geq 2.5). For AdjGR \approx 1, the nitrate RR is 2–6%. In the replacement regime (i.e., AdjGR < 0.4), the nitrate RR is between 8% and 14%. The inverse correlation between the nitrate RR and the AdjGR is shown spatially in Fig. 3. The AdjGR will be used to help assess and understand the sensitivity of the nitrate RR to input uncertainties in NH_X and TNO₃ in the sensitivity studies that follow.

In concert with the nitrate RR, the molar replacement ratio (number of moles of nitrate that replace each mole of sulfate) ranges from 0 at high AdjGRs to 1.4 at the lowest AdjGRs, with a mode at 0.8–0.9. In other words, the wintertime SO₂ reductions result in fewer than 2 mol of nitrate replacing each mole of sulfate. In an aqueous droplet, removal of ammonium sulfate is accompanied by significant liquid-water removal, which in turn increases the ammonium and nitrate molalities and shifts the NH₄NO₃ equilibrium toward the gas phase. The removal of sulfate also increases the NH₄NO₃ ionic strength fraction, which further shifts NH₄NO₃ to the gas phase (see Fig. 9.21 of Seinfeld and Pandis, 1998).

4. Sensitivity analysis bounds

In Fig. 4, comparisons of the base-case CMAQ results with daily time series of the GR, NH_X, TNO₃, and SO₄²⁻ observed at Pittsburgh (Takahama et al., 2004), illustrates the point that there can be more bias in NH_X and TNO₃ than in SO₄²⁻ and the GR at the daily or monthly level. (We do not display an AdjGR comparison because high-time-resolved NH₃ measurements were not collected at Pittsburgh.) This supports our decision to focus on the influence of the uncertainty in NH_X and TNO₃ on the nitrate RRs. While uncertainty in NH₃ emissions is the major source of NH_X uncertainty, TNO₃ has two important sources of uncertainty:

uncertainty in the reaction probability, $\gamma_{\text{N}_2\text{O}_5}$, for the heterogeneous hydrolysis of N₂O₅ to HNO₃, and uncertainty in NO_X emissions. To compare the relative influence of each uncertainty on the nitrate RR, realistic uncertainty bounds for each source of NH_X and TNO₃ uncertainty are developed below.

4.1. NH_X uncertainty: NH₃ emissions bounds

The January 2001 scaling factor from Gilliland et al. (2006) was applied to the NEI to derive the base case NH₃ emissions. This assumes changes in NH₃ emissions from 2001 to 2002 are minor. Gilliland et al. (2003) showed that after applying an inverse-modeling-based scaling factor to the NH₃ emissions in January 1990, the CMAQ results were, on average, unbiased relative to NH_X measurements collected at 53 sites across the eastern US. Yet for this group of sites, there was scatter about the 1:1 line, with 89% of the sites within symmetric factors of 2/3 (lower bound) and 3/2 (upper bound) due to spatial variability in the agreement. Given that an inverse model was also used to scale NH₃ emissions in our base-case simulations, the variability reported by Gilliland et al. (2003) provides an estimate of spatial uncertainty in the NH₃ emissions used in the present study. Furthermore, we find that domain-wide changes in NH₃ emissions result in NH_X concentration changes that are only 90% of the emission change. To compensate for this damped response of NH_X to NH₃ emission changes, the uncertainty range of the NH₃ emissions change must be increased. Thus, factors of 1.56 and 0.64 were used to create upper and lower bounds, respectively, for the NH_X uncertainty.

4.2. TNO₃ uncertainty: bounds on $\gamma_{\text{N}_2\text{O}_5}$

In CMAQv4.4, the $\gamma_{\text{N}_2\text{O}_5}$ value is calculated using the parameterization of Riemer et al. (2003).

$$\gamma_{\text{N}_2\text{O}_5} = f \times 0.02 + (1 - f) \times 0.002, \quad (4)$$

$$\text{where } f = \frac{\text{SO}_4^{\equiv} \text{mass}}{\text{SO}_4^{\equiv} \text{mass} + \text{NO}_3^- \text{mass}}.$$

Sensitivity analyzes varying $\gamma_{\text{N}_2\text{O}_5}$ have shown that the heterogeneous production of HNO₃ is a major source of the TNO₃ budget in winter (Dennis et al., 2007). Comparisons of CMAQ results with TNO₃ measurements at the Pittsburgh Supersite

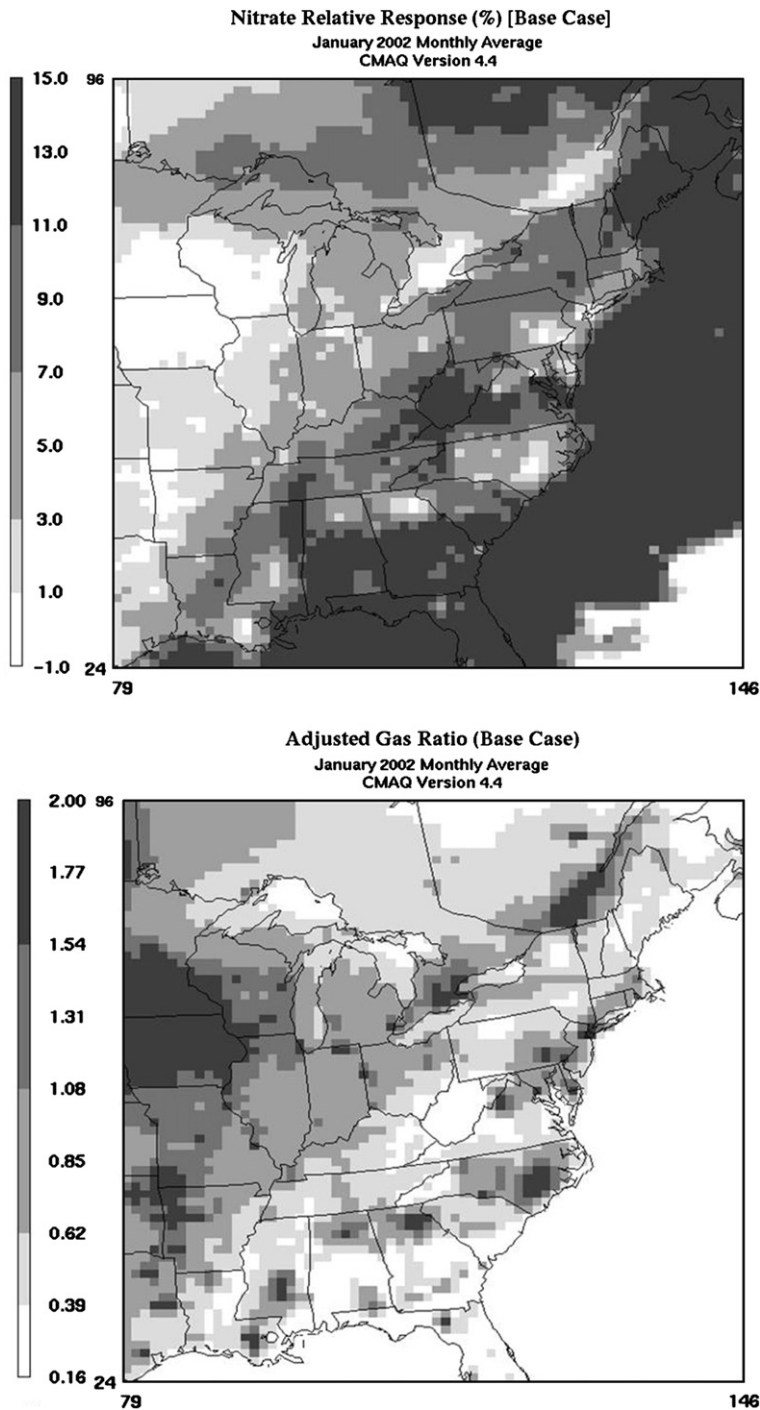


Fig. 3. Spatial tile plots of the nitrate RR and the Adjusted Gas Ratio (January 2002 monthly averages) from the base-case pair of CMAQ simulations showing the strong anti-correlation between the two fields.

and the CASTNet sites, with HNO_3 measurements at the Atlanta Supersite and model sensitivity experiments to understand these comparisons suggest that

a major fraction of CMAQ's large over-prediction of TNO_3 in the eastern US is because the values of $\gamma_{\text{N}_2\text{O}_5}$ used in CMAQ are too large. As shown in

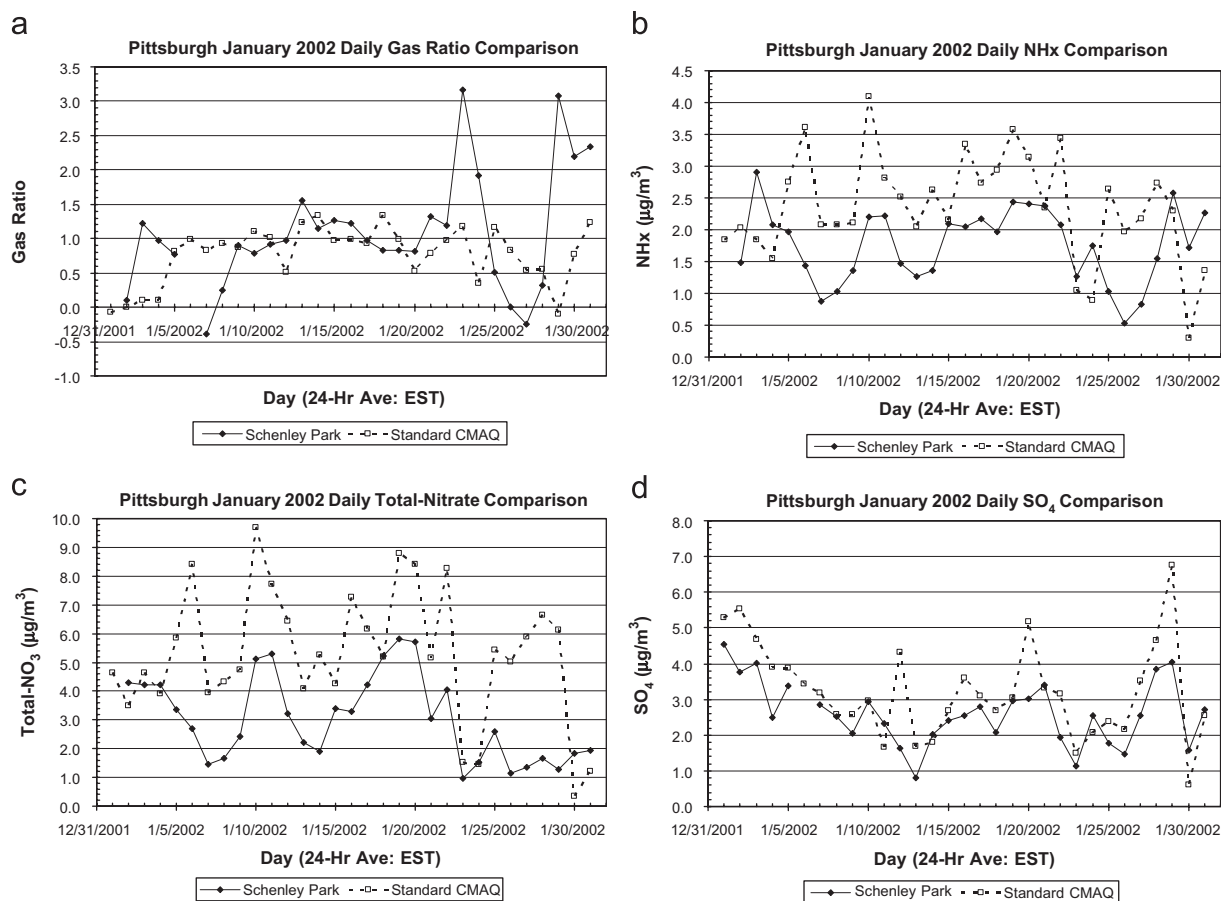


Fig. 4. Comparisons of daily-averaged CMAQ results with observations at the Pittsburgh Supersite in January 2002 for (a) the gas ratio, (b) total ammonia, (c) total nitrate, and (d) sulfate.

Fig. 5, the overprediction of TNO₃ at Pittsburgh is so significant that the base-case parameterization (i.e., Eq. (4)) may serve as the upper bound for $\gamma_{\text{N}_2\text{O}_5}$. CMAQ predictions of TNO₃ when $\gamma_{\text{N}_2\text{O}_5}$ is divided by 10 are in good agreement with CASTN et measurements during 2001 (Gilliland et al., 2006) and with Pittsburgh measurements in January 2002 (see Fig. 5). Thus, $\gamma_{\text{N}_2\text{O}_5}/10$ is judged to provide a good lower-bound estimate of $\gamma_{\text{N}_2\text{O}_5}$, to represent the uncertainty in the TNO₃ budget due to uncertainty in $\gamma_{\text{N}_2\text{O}_5}$.

4.3. TNO₃ uncertainty: NO_x emissions bounds

The NARSTO emissions assessment (NARSTO, 2005) provides a qualitative description of confidence in emissions inventories by major source sector. For purposes of this study, we attached quantitative values to these qualitative descriptors

after discussions with several scientists on the NARSTO emissions team. The following are the confidence descriptors and levels for NO_x: utilities—high confidence, $\pm 15\%$; on-road mobile sources—medium-high, $\pm 25\%$; other point sources and non-road mobile sources—medium, $\pm 50\%$ to 100%; and stationary non-point and biogenic sources—low, $\pm 100\%$ to 200%. (Although these values were developed in consultation with scientists of the NARSTO emissions inventory team, the NARSTO team has not endorsed or issued any formal quantification of their qualitative descriptors.) In the 2001 NEI, source contributions to NO_x emissions in the eastern US are roughly 24% utilities, 38% on-road mobile, 13% other point sources, 21% non-road mobile, 4% stationary non-point, and 1% other. Weighting each of these source contributions by the uncertainty values listed above yields an overall NO_x emissions uncertainty

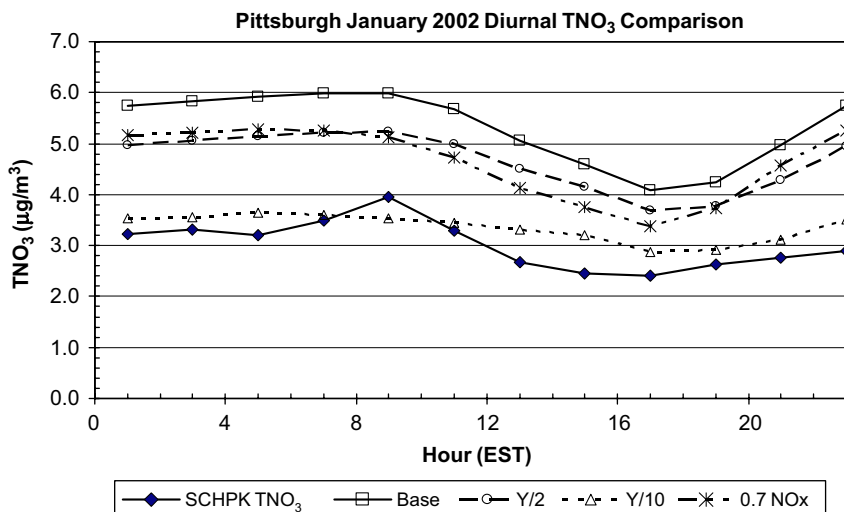


Fig. 5. Average diurnal pattern of TNO₃ at the Pittsburgh Supersite compared with four sets of CMAQ results: base-case, $\gamma_{\text{N}_2\text{O}_5}/2$, $\gamma_{\text{N}_2\text{O}_5}/10$, and $0.7 \times \text{NO}_x$ (for comparison with $\gamma_{\text{N}_2\text{O}_5}/2$).

range of $\pm 35\%$ to 57% . To be conservative, we used a factor near the midpoint of $35\text{--}57\%$. Thus, multiplicative factors of 1.43 and 0.7 were applied to the domain-wide NO_x inventory to create upper and lower bounds, respectively, for uncertainty in the TNO₃ budget due to NO_x emissions.

5. Sensitivity analysis results

In this section, results from eight pairs of CMAQ simulations are discussed: base-case, $1.56 \times \text{NH}_3$, $0.64 \times \text{NH}_3$, $\gamma_{\text{N}_2\text{O}_5}/2$, $\gamma_{\text{N}_2\text{O}_5}/4$, $\gamma_{\text{N}_2\text{O}_5}/10$, $1.43 \times \text{NO}_x$, and $0.7 \times \text{NO}_x$. In each simulation pair, one run is conducted using the January 2002 SO_2 inventory and the other with a 25% SO_2 reduction. Ten CMAQ grid cells in cities that cover a broad range of AdjGRs and nitrate RRs are selected for detailed exploration. This maintains the urban focus and allows a concise, yet comprehensive, investigation of the sensitivity of nitrate RRs to errors in the NH_x and TNO₃ budgets. A variety of results from the CMAQ simulations are provided in Tables 1–4. In these tables, concentration changes produced by the SO_2 emission reduction are denoted by a “ Δ ” in front of the species name. Eq. (3), the best-fit equation, is applied to AdjGRs obtained from CMAQ simulations that used the base-case SO_2 inventory, to produce a quantitative expectation of the nitrate RR in each simulation pair. The maximum ranges of CMAQ-realized nitrate RRs from each sensitivity study (i.e., NH_3 , $\gamma_{\text{N}_2\text{O}_5}$, and NO_x) are used to compare the relative importance

of errors in each uncertain input. Table 1 provides results for the base case.

5.1. Nitrate RR sensitivity to NH_x uncertainty

As shown in Table 2, the nitrate RR responds substantially to changes in NH_3 emissions, decreasing (increasing) as NH_x increases (decreases). The net effect of NH_3 emission uncertainties on the nitrate RR is larger ($\pm 3\%$ to 5% absolute difference) at cities with low AdjGRs (e.g., Richmond, Columbus, Atlanta) and smaller ($\pm 1\%$ to 2% absolute difference) at high AdjGRs. The sigmoid relationship in Eq. (3), used only as a qualitative indicator, predicts fairly well the magnitude and trend of the nitrate RR sensitivity to the NH_x uncertainty, especially for AdjGRs below 1.1 (Table 2). At cities with the highest AdjGRs (e.g., Chicago, New York City), the sigmoid relationship overpredicts the effect of the increase in NH_3 emissions (to high- NH_x) on nitrate RRs.

At all 10 cities, the relative change in NH_x follows the NH_3 emissions change—though slightly damped—and is symmetric about the base-case. Relative changes in NO_3^- are similar to the NH_3 emissions changes in the replacement regime. As the particulate fraction of TNO₃ increases (decreases), TNO₃ increases (decreases) because particulate NO_3^- deposits more slowly than HNO_3 (g). Due to this feedback of NH_3 emissions on TNO₃, the AdjGR is less sensitive to NH_3 emission changes than it would have been if an artificial change in

Table 1

Values of Adjusted GR, RRs, species concentrations, and absolute change in nitrate concentrations due to the 25% SO₂ emission reductions at 10 selected cities in the base-case simulations

	Richmond	Columbus	Nashville	Pittsburgh	Atlanta	Philadelphia	St. Louis	South Philadelphia	Chicago	New York City
Adjusted GR	0.57	0.79	0.87	0.90	1.07	1.19	1.47	1.64	2.50	2.73
NO ₃ RR (%)	9.31	5.19	5.76	5.15	5.02	2.32	1.00	0.88	0.36	0.09
NO ₃ RR (AdjGR)	10.89	7.84	6.89	6.59	4.90	4.00	2.54	1.96	0.68	0.54
NH _x (μg m ⁻³)	1.80	2.34	2.25	2.48	3.03	3.53	3.08	4.67	5.41	6.47
TNO ₃ (μg m ⁻³)	4.91	6.49	5.28	5.62	5.64	7.34	5.45	7.57	5.88	6.85
SO ₄ ²⁻ (μg m ⁻³)	2.97	2.61	3.02	3.26	3.62	2.89	2.26	3.05	3.49	3.31
SO ₄ RR (%)	-13.9	-12.8	-13.4	-11.8	-10.9	-11.4	-10.1	-10.7	-6.8	-9.7
NO ₃ ⁻ (μg m ⁻³)	2.32	4.49	3.45	4.23	3.92	6.11	4.82	7.04	5.79	6.73
ΔNO ₃ ⁻ (μg m ⁻³)	0.22	0.23	0.20	0.22	0.20	0.14	0.05	0.06	0.02	0.01

NO₃ RR (AdjGR) is computed from Eq. (3).

NH_x concentrations had been imposed. Note that the NH₃ emission changes produce no feedback on ΔSO₄²⁻ values.

5.2. Nitrate RR sensitivity to TNO₃: γ_{N₂O₅} uncertainty

The nitrate RR varies very little in the γ_{N₂O₅} sensitivity study (Table 3). The absolute change from the base-case is (except in Richmond) <1 percentage point. Most notable is that the expected decline in nitrate RR as γ_{N₂O₅} is scaled down (and AdjGR becomes larger) stops and reverses between γ_{N₂O₅}/2 and γ_{N₂O₅}/10 (again except in Richmond). This behavior constrains the overall sensitivity of the nitrate RR to changes in γ_{N₂O₅} and was initially puzzling, because the base-case sigmoid equation suggests that the RR should decline monotonically with TNO₃. Model sensitivity analyses indicate the key reason for this constraint on the nitrate RR is the inhibition of N₂O₅ hydrolysis by particulate NO₃⁻ inherent in the Riemer parameterization of *f* (see Eq. (4)). This inhibition is supported empirically by measurements from the 2004 ICARTT field study (Brown et al., 2006). The result is that when SO₄²⁻ decreases in response to a 25% SO₂ emission control, *f* and, therefore, γ_{N₂O₅} also decrease, thereby decreasing TNO₃ production. An extra pair of CMAQ simulations with γ_{N₂O₅} held at a constant value of 0.011 suggests that the Riemer formulation has the effect of depressing the base-case nitrate RR by an average of 1.1 percentage points in the 10 selected cities (see Table 3) and an average of 0.83 percentage points over all 1822 grid cells. The value of 0.011 was the average across cells, with most cells

close to this value. The “Riemer effect” is most significant at high AdjGRs, even leading to negative RRs in New York City. No negative RRs were found in the extra sensitivity with γ_{N₂O₅} held constant. As the base-case parameterization of γ_{N₂O₅} is scaled down by factors of 2, 4, and 10, the Riemer effect is mitigated because NO₃⁻ and the fraction of TNO₃ coming from heterogeneous production decrease. As a result, the decreasing nitrate RR reverses by the γ_{N₂O₅}/10 sensitivity.

5.3. Nitrate RR sensitivity to TNO₃: NO_x uncertainty

As shown in Table 4, the nitrate RR is moderately sensitive to uncertainties in NO_x emissions. An increase in NO_x emissions results in lower nitrate RRs, and vice versa, with the largest effects on RRs found at cities with low AdjGRs (e.g., Richmond, Columbus, and Pittsburgh). SO₄²⁻ and ΔSO₄²⁻ decrease as NO_x emissions increase, and vice versa. These sulfate changes dominate the sensitivity of the nitrate RR to NO_x emissions, and are due to a non-linear feedback between NO_x emissions and SO₄²⁻ production that is regional in nature (Pinder et al., this issue). The effect of this feedback on nitrate RRs is not captured in the base-case sigmoid equation, because the feedback has little impact on the AdjGRs (see Table 4).

In winter, the regional atmosphere is VOC-limited, in large part due to the absence of isoprene emissions. The atmospheric transition in fall from NO_x- to VOC-limited regimes has been observed at Shenandoah National Park (Jacob et al., 1995). This means that when NO_x emissions are reduced, O₃

Table 2

Values of Adjusted GR, nitrate RRs, species concentrations, and absolute change in species concentrations due to the 25% SO₂ emission reductions at 10 cities in the NH_x sensitivity study

NH _x sensitivity	Richmond	Columbus	Nashville	Pittsburgh	Atlanta	Philadelphia	St. Louis	South Philadelphia	Chicago	New York City
Adjusted GR										
High-NH _x	0.89	1.09	1.23	1.23	1.59	1.65	1.98	2.31	3.49	3.83
Base	0.57	0.79	0.87	0.90	1.07	1.19	1.47	1.64	2.50	2.73
Low-NH _x	0.30	0.50	0.53	0.56	0.60	0.79	1.05	1.10	1.77	1.90
NO ₃ RR (%) CMAQ-realized										
High-NH _x	5.45	2.23	3.22	2.63	1.97	0.55	-0.16	-0.43	-0.21	-0.25
Base	9.31	5.19	5.76	5.15	5.02	2.32	1.00	0.88	0.36	0.09
Low-NH _x	14.4	9.09	9.36	8.83	9.65	5.28	3.08	3.67	1.83	1.21
NO ₃ RR (%) Sigmoid equation										
High-NH _x	6.67	4.70	3.72	3.69	2.12	1.92	1.22	0.83	0.28	0.22
Base	10.89	7.84	6.89	6.59	4.90	4.00	2.54	1.96	0.68	0.54
Low-NH _x	14.04	11.84	11.47	11.03	10.53	7.94	5.05	4.67	1.63	1.36
NH _x (μg m ⁻³)										
High-NH _x	2.64	3.41	3.32	3.62	4.42	5.15	4.45	6.85	8.01	9.69
Base	1.80	2.34	2.25	2.48	3.03	3.53	3.08	4.67	5.41	6.47
Low-NH _x	1.21	1.58	1.51	1.66	2.04	2.39	2.11	3.14	3.65	4.34
TNO ₃ (μg m ⁻³)										
High-NH _x	6.02	7.85	6.40	7.02	6.77	8.53	6.40	8.65	6.72	7.81
Base	4.91	6.49	5.28	5.62	5.64	7.34	5.45	7.57	5.88	6.85
Low-NH _x	4.17	5.42	4.44	4.53	4.77	6.25	4.46	6.53	4.91	5.93
ΔSO ₄ ²⁻ (μg m ⁻³)										
High-NH _x	-0.42	-0.34	-0.41	-0.39	-0.40	-0.34	-0.24	-0.33	-0.25	-0.33
Low-NH _x	-0.41	-0.33	-0.40	-0.38	-0.39	-0.33	-0.23	-0.33	-0.24	-0.32
NO ₃ ⁻ (μg m ⁻³)										
High-NH _x	4.11	6.74	5.22	6.30	5.87	8.07	6.06	8.50	6.68	7.77
Low-NH _x	1.07	2.51	1.92	2.34	2.06	3.94	3.34	5.04	4.60	5.55
ΔNO ₃ ⁻ (μg m ⁻³)										
High-NH _x	0.22	0.15	0.17	0.17	0.12	0.04	-0.01	-0.04	-0.01	-0.02
Low-NH _x	0.15	0.23	0.18	0.21	0.20	0.21	0.10	0.18	0.08	0.07

High-NH_x = 1.56 × base; low-NH_x = 0.64 × base.

will increase. In the regional environment, O₃ is the major source of new OH radicals (Jeffries, 1995). Thus, the increase of O₃ will increase the oxidizing capacity of the atmosphere and increase the rate of SO₂ oxidation to sulfate. (Conversely, the opposite effect will occur when NO_x emissions are increased.) When NO_x emissions are reduced to 0.7 times the base-case, CMAQ results show a regional O₃ increase of 11–25%. Urban O₃ increases more: 50–75%. Sulfate, therefore, increases by 8–12%, but urban values change the same percentage as rural values. When NO_x emissions are increased to 1.43 times the base case, CMAQ results show that regional O₃ decreases 15–25%, and urban O₃ decreases 49–63%. Sulfate decreases by 7–12%;

again urban values change the same percentage as rural values. The sulfate responses to symmetric changes in NO_x emissions are symmetric about the base-case. The regional patterns of increase and decrease in SO₄²⁻ and O₃ (not shown) are also quite symmetric.

In the high-NO_x sensitivity simulations, the increases in NO₃⁻ and, therefore, free NH₃ due to the decrease in SO₄²⁻ are just slightly larger than the increase in TNO₃, and the converse is true in the low-NO_x simulations. Thus, the AdjGR is changed very little by the NO_x emissions changes. Moreover, Fig. 5 shows that TNO₃ concentrations in the low-NO_x case are similar to those in the γ_{N₂O₅}/2 case. The fact that the nitrate RR changes in opposite

Table 3

Values of Adjusted GR, nitrate RR, absolute percentage point difference due to “Riemer effect”, species concentrations, and absolute change in nitrate concentration due to the 25% SO₂ emission reductions at 10 selected cities in the $\gamma_{\text{N}_2\text{O}_5}$ sensitivity study

$\gamma_{\text{N}_2\text{O}_5}$ sensitivity	Richmond	Columbus	Nashville	Pittsburgh	Atlanta	Philadelphia	St. Louis	South Philadelphia	Chicago	New York City
Adjusted GR										
Base	0.57	0.79	0.87	0.90	1.07	1.19	1.47	1.64	2.50	2.73
$\gamma_{\text{N}_2\text{O}_5}/2$	0.64	0.88	0.95	0.99	1.18	1.35	1.63	1.89	2.82	3.14
$\gamma_{\text{N}_2\text{O}_5}/4$	0.71	0.99	1.04	1.11	1.30	1.56	1.82	2.22	3.19	3.67
$\gamma_{\text{N}_2\text{O}_5}/10$	0.81	1.14	1.17	1.27	1.47	1.86	2.06	2.71	3.68	4.44
NO₃ RR (%)										
Base	9.31	5.19	5.76	5.15	5.02	2.32	1.00	0.88	0.36	0.09
$\gamma_{\text{N}_2\text{O}_5}/2$	8.50	4.58	5.48	4.68	4.64	1.75	0.87	0.34	0.23	−0.16
$\gamma_{\text{N}_2\text{O}_5}/4$	8.30	4.25	5.34	4.42	4.41	1.68	0.83	0.17	0.36	−0.07
$\gamma_{\text{N}_2\text{O}_5}/10$	7.91	4.33	5.60	4.67	4.45	1.99	1.19	0.64	0.84	0.57
Magnitude of “Riemer reduction” of NO ₃ RR (abs) ^a	−0.81	−0.65	−0.80	−0.85	−0.93	−1.25	−1.13	−1.68	−1.35	−1.75
TNO₃ (μg m^{−3})										
Base	4.91	6.49	5.28	5.62	5.64	7.34	5.45	7.57	5.88	6.85
$\gamma_{\text{N}_2\text{O}_5}/2$	4.29	5.62	4.69	4.91	5.01	6.26	4.76	6.42	5.11	5.88
$\gamma_{\text{N}_2\text{O}_5}/4$	3.71	4.80	4.13	4.21	4.41	5.25	4.14	5.35	4.43	4.96
$\gamma_{\text{N}_2\text{O}_5}/10$	3.11	3.96	3.53	3.48	3.79	4.25	3.53	4.28	3.77	4.05
NO₃[−] (μg m^{−3})										
Base	2.32	4.49	3.45	4.23	3.92	6.11	4.82	7.04	5.79	6.73
$\gamma_{\text{N}_2\text{O}_5}/2$	2.17	4.13	3.15	3.84	3.58	5.41	4.23	6.06	5.03	5.79
$\gamma_{\text{N}_2\text{O}_5}/4$	2.00	3.70	2.82	3.40	3.22	4.66	3.70	5.10	4.35	4.89
$\gamma_{\text{N}_2\text{O}_5}/10$	1.78	3.15	2.44	2.86	2.82	3.87	3.16	4.10	3.70	3.99
ΔNO₃[−] (μg m^{−3})										
Base	0.22	0.23	0.20	0.22	0.20	0.14	0.05	0.06	0.02	0.01
$\gamma_{\text{N}_2\text{O}_5}/2$	0.18	0.19	0.17	0.18	0.17	0.09	0.04	0.02	0.01	−0.01
$\gamma_{\text{N}_2\text{O}_5}/4$	0.17	0.16	0.15	0.15	0.14	0.08	0.03	0.01	0.02	0.00
$\gamma_{\text{N}_2\text{O}_5}/10$	0.14	0.14	0.14	0.13	0.13	0.08	0.04	0.03	0.03	0.02

^aCalculated as the difference in the base case NO₃ RR minus the NO₃ RR for $\gamma_{\text{N}_2\text{O}_5}$ held constant at 0.011.

directions when NO_X is decreased than when $\gamma_{\text{N}_2\text{O}_5}$ is divided by 2 suggests the change in TNO₃ is having a minor effect and the change in ΔSO₄[−] is having the dominant effect. The increase (decrease) in NO₃[−] is enhanced for high (low) NO_X because SO₄[−] decreases (increases), leaving more (less) NH₃ to produce nitrate. For high (low) NO_X, ΔNO₃[−] decreases (increases) because ΔSO₄[−] decreases by ≈15% (increases by ≈15%). Both changes work together to decrease (increase) the nitrate RR for high (low) NO_X. The importance of the changes in ΔSO₄[−] can be illustrated by normalizing the nitrate RRs in the high- and low-NO_X sensitivities by the ratio of ΔSO₄[−] to the base-case ΔSO₄[−]. This brings

the nitrate RRs obtained from the high- and low-NO_X simulations closer together, and into the range of RRs obtained in the $\gamma_{\text{N}_2\text{O}_5}$ sensitivity study (compare bottom rows of Table 4 with top row of Table 5). Thus, the NO_X emission inputs do affect the nitrate RR, but most of the sensitivity in RR values results from the non-linear interaction between NO_X and SO₄[−] production.

6. Discussion and conclusions

The maximum absolute effects of each model input (NH₃ emissions, $\gamma_{\text{N}_2\text{O}_5}$ scaling factor, and NO_X emissions) on nitrate RRs are compared in

Table 4

Values of Adjusted GR, nitrate RRs, species concentrations, and changes in concentrations due to the 25% SO₂ emissions reduction at 10 selected cities for the NO_x sensitivity study

NO _x sensitivity	Richmond	Columbus	Nashville	Pittsburgh	Atlanta	Philadelphia	St. Louis	South Philadelphia	Chicago	New York City
Adjusted GR										
High-NO _x	0.56	0.77	0.82	0.89	1.00	1.21	1.33	1.64	2.26	2.72
Base	0.57	0.79	0.87	0.90	1.07	1.19	1.47	1.64	2.50	2.73
Low-NO _x	0.61	0.86	0.96	0.94	1.18	1.21	1.65	1.74	2.83	2.81
NO ₃ RR (%)										
High-NO _x	7.31	4.09	4.76	3.99	4.06	1.67	0.78	0.55	0.22	−0.03
Base	9.31	5.19	5.76	5.15	5.02	2.32	1.00	0.88	0.36	0.09
Low-NO _x	11.37	6.09	6.48	6.29	6.00	2.83	1.34	1.11	0.54	0.31
SO ₄ [−] (μg m ^{−3})										
High-NO _x	2.69	2.35	2.75	2.99	3.32	2.68	2.08	2.82	3.29	3.09
Base	2.97	2.61	3.02	3.26	3.62	2.89	2.26	3.05	3.49	3.31
Low-NO _x	3.29	2.87	3.33	3.56	3.92	3.18	2.43	3.34	3.70	3.58
ΔSO ₄ [−] (μg m ^{−3})										
High-NO _x	−0.35	−0.28	−0.35	−0.32	−0.33	−0.27	−0.19	−0.27	−0.21	−0.27
Base	−0.41	−0.33	−0.41	−0.38	−0.39	−0.33	−0.23	−0.33	−0.24	−0.32
Low-NO _x	−0.47	−0.39	−0.46	−0.44	−0.46	−0.39	−0.26	−0.39	−0.27	−0.38
NO ₃ [−] (μg m ^{−3})										
High-NO _x	2.62	4.86	3.86	4.53	4.44	6.19	5.58	7.19	6.59	6.81
Base	2.32	4.49	3.45	4.23	3.92	6.11	4.82	7.04	5.79	6.73
Low-NO _x	1.95	3.96	2.94	3.75	3.30	5.73	4.04	6.43	4.91	6.42
ΔNO ₃ [−] (μg m ^{−3})										
High-NO _x	0.19	0.20	0.18	0.18	0.18	0.10	0.04	0.04	0.01	0.00
Base	0.22	0.23	0.20	0.22	0.20	0.14	0.05	0.06	0.02	0.01
Low-NO _x	0.22	0.24	0.19	0.24	0.20	0.16	0.05	0.07	0.03	0.02
NO ₃ RR (ΔSO ₄ [−] constant) ^a (%)										
High-NO _x	8.65	4.89	5.58	4.72	4.85	2.03	0.93	0.67	0.25	−0.04
Low-NO _x	9.95	5.29	5.69	5.44	5.16	2.38	1.17	0.94	0.47	0.26

High-NO_x = 1.43 × base; low-NO_x = 0.70 × base.

^aNO₃ RR normalized by the ratio of the high- or the low-NO_x ΔSO₄[−] to the base-case ΔSO₄[−].

Table 5

Comparison across the three sensitivities of the maximum absolute effect (%) of each perturbed model input on nitrate RRs

Cross-sensitivity comparison	Richmond	Columbus	Nashville	Pittsburgh	Atlanta	Philadelphia	St. Louis	South Philadelphia	Chicago	New York City
Absolute RR change										
γ _{N₂O₅} max–min RR	1.4	0.9	0.4	0.7	0.6	0.6	0.4	0.7	0.6	0.7
NO _x max–min RR	4.1	2.0	1.7	2.3	1.9	1.2	0.6	0.6	0.3	0.3
NH _x max–min RR	8.9	6.9	6.1	6.2	7.7	4.7	3.2	4.1	2.0	1.5
Reference: base-case RR	9.31	5.19	5.76	5.15	5.02	2.32	1.00	0.88	0.36	0.09

The base-case RR (%) at all 10 selected cities is repeated for reference.

Table 5 (ordered from lowest to highest effect). Of the three, the uncertainty in NH_x is by far the most important contributor to uncertainty in the nitrate RR. The uncertainty in NO_x emissions is a less

important contributor, and the uncertainty in γ_{N₂O₅} is a negligible contributor. In the NH₃ and NO_x sensitivity studies, the largest absolute uncertainty is associated with the smallest AdjGRs. Due to the

Riemer effect, the $\gamma_{\text{N}_2\text{O}_5}$ sensitivity study exhibits no such trend.

The NO_x sensitivity results indicate that errors $> \pm 15\%$ in the SO_4^{2-} concentrations (due to transformation and transport errors) are important in predicting nitrate RRs. The CMAQ model evaluation by Eder and Yu (2006) suggest that SO_4^{2-} errors are larger than this, even though SO_2 emissions have less uncertainty than the three model inputs perturbed in this work (NARSTO, 2005). Further study of SO_4^{2-} spatial uncertainties in the 3-D model is warranted so that their impact on nitrate RRs may be determined. Such a study will be more complicated than the present investigation because a double uncertainty involving SO_2 emission errors superimposed on the fixed SO_2 emission reduction (e.g., 25%) may be required.

It is important to carry out sensitivity studies within a full chemical transport model because it is the full model, with all of its dynamic feedbacks, which is being used to support air quality management decisions. In this study, several of the dynamic feedbacks within the full atmospheric fine-particle system—such as changes in TNO_3 dry removal due to effects of NH_3 on nitrate partitioning, inhibiting effects of particulate NO_3^- on the heterogeneous production of nitrate, and the impacts of NO_x emission changes on O_3 and SO_4^{2-} —have been shown to be important. Deposition was also found to be important in an investigation with equilibrium models (Vayenas et al., 2005). Further study with instrumented 3-D models (in which results of intermediate process steps are output) is needed to help dissect and understand the complexities inherent in air quality model results.

The base-case simulation results indicate that sulfate removed by SO_2 emission controls is never completely replaced by nitrate during winter in the eastern US. This is useful information. Given the relationship identified between the nitrate RR and AdjGR in the base-case, this study indicates that the AdjGR should be a useful screening tool to test whether model results for present-day conditions are in the appropriate inorganic response regime to project future-year nitrate RRs. This relationship should be tested for applicability to other seasons.

This work has shown that it is crucial to have measurements of HNO_3 and NH_3 , in addition to fine-particle measurements, to estimate and track RRs and their uncertainties via measurements and 3-D models, and to compare the model-inferred

state of the aerosol system with the observed state. No national monitoring network in the US has this capability. This is a serious deficiency that must be addressed if the air quality community is to knowledgeably assess model physics and uncertainties and track changes in atmospheric concentrations.

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References

- Ansari, A.S., Pandis, S.N., 1998. Response of inorganic PM to precursor concentrations. *Environmental Science & Technology* 32, 2706–2714.
- Blanchard, C.L., Roth, P.M., Tanenbaum, S.J., Ziman, S.D., Seinfeld, J.H., 2000. The use of ambient measurements to identify which precursor species limit aerosol nitrate formation. *Journal of the Air & Waste Management Association* 50, 2073–2084.
- Boylan, J.W., Odman, M.T., Wilkinson, J.G., Russell, A.G., Doty, K.G., Norris, W.B., McNider, R.T., 2002. Development of a comprehensive, multiscale “one-atmosphere” modeling system: application to the Southern Appalachian Mountains. *Atmospheric Environment* 36, 3721–3734.
- Brown, S.S., Ryerson, T.B., Wollny, A.G., Brock, C.A., Peltier, R., Sullivan, A.P., Weber, R.J., Dube, W.P., Trainer, M., Meagher, J.F., Fehsenfeld, F.C., Ravishankara, A.R., 2006. Variability in nocturnal nitrogen oxide processing and its role in regional air quality. *Science* 311, 67–70.
- Dennis, R.L., Roselle, S.J., Gilliam, R., Arnold, J., 2007. High time-resolved comparisons for in-depth probing of CMAQ fine-particle and gas predictions. In: Borrego, C., Norman, A.-L. (Eds.), *Air Pollution Modeling and Its Application XVII*. Springer Science+Business, New York, NY, pp. 515–524.
- Eder, B.K., Yu, S., 2006. A performance evaluation of the 2004 release of Models-3 CMAQ. *Atmospheric Environment* 40, 4811–4824.

- Gilliam, R.C., Hogrefe, C., Rao, S.T., 2006. New methods for evaluating meteorological models used in air quality applications. *Atmospheric Environment* 40, 5073–5086.
- Gilliland, A.B., Dennis, R.L., Roselle, S.J., Pierce, T.E., 2003. Seasonal NH₃ emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method. *Journal of Geophysical Research—Atmospheres* 108 (D15), 4477.
- Gilliland, A.B., Appel, K.W., Pinder, R., Dennis, R.L., 2006. Seasonal NH₃ emissions for the continental United States: inverse model estimation and evaluation. *Atmospheric Environment* 40, 4986–4998.
- Jacob, D.J., Heikes, B.G., Dickerson, R.R., Artz, R.S., Keene, W.C., 1995. Seasonal transition from NO_x- to hydrocarbon-limited conditions for ozone production over the eastern United States in September. *Journal of Geophysical Research* 100 (5), 9315–9324.
- Jeffries, H.E., 1995. Photochemical air pollution. In: Singh, H.B. (Ed.), *Composition, Chemistry, and Climate of the Atmosphere*. Van Nostrand-Reinhold, New York, pp. 308–348.
- Khlystov, A., Stanier, C.O., Takahama, S., Pandis, S.N., 2005. Water content of ambient aerosol during the Pittsburgh Air Quality Study. *Journal of Geophysical Research* 110, D07S10.
- Mebust, M.R., Eder, B.K., Binkowski, F.S., Roselle, S.J., 2003. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component, 2. Model evaluation. *Journal of Geophysical Research* 108 (D6), 4184.
- NARSTO, 2005. Improving emission inventories for effective air quality management across North America: a NARSTO assessment. Report No. NARSTO-05-001, Pasco, Washington, June 2005.
- Pinder, R.W., Dennis, R.L., Bhavsar, P.V. Observable indicators of the sensitivity of PM_{2.5} nitrate to emission reductions, Part I: derivation of the adjusted gas ratio and applicability at regulatory-relevant time scales. *Atmospheric Environment*, this issue, doi:10.1016/j.atmosenv.2007.10.039.
- Rood, M.J., Shaw, M.A., Larson, T.V., Covert, D.S., 1989. Ubiquitous nature of ambient metastable aerosol. *Nature* 336, 537–539.
- Riemer, N., Vogel, H., Vogel, B., Schell, B., Ackermann, I., Kessler, C., Hass, H., 2003. Impact of the heterogeneous hydrolysis of N₂O₅ on chemistry and nitrate aerosol formation in the lower troposphere under photochemical conditions. *Journal of Geophysical Research* 108 (D4), 4144.
- Seigneur, C., 2001. Current status of air quality models for particulate matter. *Journal of the Air & Waste Management Association* 51, 1508–1521.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics*. Wiley, New York.
- Takahama, S., Witting, A.E., Vayenas, D.V., Davidson, C.I., Pandis, S.N., 2004. Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study. *Journal of Geophysical Research* 109, D16S06.
- US Environmental Protection Agency, 2007. Guidance for Demonstrating Attainment of Air Quality Goals for PM_{2.5} and Regional Haze, Office of Air Quality Planning and Standards, Research Triangle Park, NC. <<http://www.epa.gov/ttn/scram/guidance/guide/final-03-pm-rh-guidance.pdf>>
- Vayenas, D.V., Takahama, S., Davidson, C.I., Pandis, S.N., 2005. Simulation of the thermodynamics and removal processes in the sulfate-ammonia-nitric acid system during winter: implications for PM_{2.5} control strategies. *Journal of Geophysical Research* 110, D07S14.
- West, J.J., Ansari, A.S., Pandis, S.N., 1999. Marginal PM_{2.5}: nonlinear aerosol mass response to sulfate reductions in the Eastern United States. *Journal of the Air & Waste Management Association* 49, 1415–1424.
- Yu, S., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., 2005. An assessment of the ability of 3-D air quality models with current thermodynamic equilibrium models to predict aerosol NO₃⁻. *Journal of Geophysical Research* 110, D07S13.